A POLAROGRAPHIC STUDY OF SOME INORGANIC COMPLEX IONS

BY

EDWARD IRVIN ONSTOTT

B.S., University of Illinois, 1944
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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A POLAROGRAPHIC STUDY OF SOME INORGANIC COMPLEX IONS

Several complex ions of copper were studied by means of the dropping mercury electrode in order to determine the effect of specific coördinating agents on the stability of the cuprous and cupric oxidation states. Determination of the formulae of the complexes and calculation of their dissociation constants was possible in most cases, as the electrode reactions were reversible. Lingane (1) and von Stackelberg (6) have shown that the dropping mercury electrode is applicable to the study of complex ions which are reduced reversibly.

The reduction of tetrachloroplatinate (II) ion at the dropping mercury electrode was studied in detail. It appeared that the complex ion, adsorbed on the electrode surface, underwent reduction of small values of applied e.m.f., but was desorbed before the normal irreversible reduction process occurred. The observation that tetrachloroplatinate (II) ion is reduced at the dropping mercury electrode is in contradiction to the finding of Willis (7), who reported that it is not reduced.

Experimental

Both the Sargent Model XI and the Sargent Model XXI polarographs were used to record polarograms. Potentials were measured to the nearest millivolt with a Leeds and Northrup potentiometer. A Beckman pH meter was used for pH measurements. A type E electrode was used to measure the pH of strongly alkaline solutions. The bulb type saturated calomel electrode was used as a reference electrode, and an H-cell with a temporary plug of 3% agar in 0.1N or 0.5N potassium nitrate was employed for the study of the complexes of copper. A special H-cell having a fine sintered glass plug in the connecting arm was used for studying tetrachloroplatinate (II) ion.

Reversibility of the electrode reactions was tested by determining the slopes of plots of log $(i_d - i)/i$ *vs.* E. In most cases the half-wave potentials were taken directly from the logarithmic plots.

Discussion

Cupric complexes of ethylenediamine, propylenediamine, and diethylenetriamine were found to be reduced reversibly in one step to copper amalgam. The reduction of the glycine complex directly to the amalgam was reversible in the pH range of 6 to 8 when a phosphate buffer was used.

Cupric ion in the presence of pyrophosphate at a pH of 3.6 to 5.3 was found to be reduced reversibly in one step when an acetate buffer was used. However, at higher pH values, the reduction proceeded in two steps, the ratio of the heights of the two waves varying with pH. Reversibility of the electrode reactions was not exhibited. The occurrence of the double wave was attributed to the reduction of two different complex ions in sluggish equilibrium, one being more easily reduced than the other. This interpretation differs from that of Rogers and Reynolds (5), who attributed the double wave to the reduction of a single complex ion, one electron being added in each electrode reaction.

The dipyridyl complex of copper was found to be reduced in two steps. In the first step the corresponding cuprous complex was formed, and in the second step further reduction to the amalgam occurred. Both electrode reactions were reversible.

In the presence of thiourea, the cuprous complex ion was found to be reduced reversibly in one step to the amalgam. A study of the cupric complex was not possible, as it does not exist under ordinary conditions.

The equations derived by Lingane (1), which relate the half-wave potentials of the simple and complex ions and the concentration of excess complexing agent to the formula and dissociation constant of the complex ion, were used to deter-

mine the formulae of the complex ions and to calculate their dissociation constants. Plots of the half-wave potentials of the complex ions *versus* the logarithm of the concentration of excess complexing agents gave slopes indicative of the number of coördinated groups. Formulae which were determined and dissociation constants which were calculated, assuming the ratio of the diffusion coefficients and the ratio of the activity coefficients of the ions to be unity and taking the activity of the complexing agent to be equal to its concentration, are listed in the table below.

Formula of complex ion	Conc. of excess complexing agent	Calculated dissociation constant
$[Cu\ en_2]^{++}$	40 to 2000-fold	1.9×10^{-20}
$[Cu\ pn_2]^{++}$	40 to 2000-fold	6.8×10^{-21}
$[Cu\ dien_2]^{++}$	40 to 2000-fold	1.4×10^{-21}
$[Cu\ gly_2]^{o}$	1 to 10-fold	7.9×10^{-16}
$[Cu\ dipy_3]^{++}$	50 to 200-fold	1.4×10^{-18}
$[Cu\ dipy_2]^{+}$	50 to 200-fold	6.3×10^{-15}
$[Cu\ tu_4]^{+}$	50 to 1600-fold	4.1×10^{-16}
$[Cu(HP_2O_7)_2]^{-4}$	> 1-fold	1×10^{-10}
$[Cu(HP_2O_7)]^{-1}$	< 1-fold	4×10^{-7}

Identification of the pyrophosphate complex ions of copper present at pH values greater than 5 was not possible from half-wave potential data, but evidence for the existence of pyrophosphate(monohydrogenpyrophosphate)cuprate (II) ion in the pH range of 7 to 10 was obtained from diffusion current data. The diffusion current constant of bis(monohydrogenpyrophosphate)cuprate (II) ion was found to be about 11% greater than that for the complex ion which exists at a pH of 7 to 10. This difference was attributed to a difference in charges of the two complex ions, assuming their equivalent ionic conductance to be the same. The diffusion current constant for an ion of charge minus four should be about 10% greater than that for an ion of equal equivalent ionic conductance having a charge of minus five, as the diffusion current constant varies inversely with the square root of the

charge (3).

By determining the pH at which cupric hydroxide was precipitated from solutions containing the pyrophosphate complex ion and excess pyrophosphate ion, it was possible to evaluate an equilibrium constant for the reaction of the complex ion with hydroxide ion to form cupric hydroxide. The complex ion found to be in equilibrium with cupric hydroxide at the pH it is precipitated was hydroxopyrophosphatecuprate (II) ion. Its dissociation constant was calculated to be 2×10^{-16}.

Bis (ethylenediamine) copper (II) ion, normally reduced directly to the amalgam, was found to be reduced to two separate steps when a large excess of ethylenediamine and thiourea, which stabilizes only cuprous ion, were present. In the first step the cupric complex ion was reduced irreversibly to the cuprous complex ion, but further reduction to copper amalgam in the second step took place reversibly, the potential being determined by tetrathiourea copper (I) ion. The reduction of bis (ethylenediamine) copper (II) ion to tetrathiourea copper (I) ion is unusual in that the coördinated ethylenediamine molecules must be replaced by thiourea molecules simultaneously as the electron is added.

Tetrachloroplatinate (II) ion was shown to be reduced at the dropping mercury electrode at small values of applied e.m.f., giving a wave which showed a decreasing current region at more negative potentials. The current decreased to a minimum value before increasing again due to the normal irreversible reduction of tetrachloroplatinate (II) ion. The decrease in current as the potential was increased was shown to be caused by a desorption process, adsorption of the reducible ion being a necessary condition for reduction to occur. As the current for the reduction of the adsorbed reducible ion was controlled by diffusion, an equation describing the desorption wave could be derived by considering the thermodynamics of adsorption equilibrium. The equation which was derived is

$$E = E_{1/2}^{d} - RT/2F \ln A - RT/2F \ln (i_d - i)/i,$$

where A represents the average area of adsorption and other symbols are those conventionally used in polarography. Reversibility of the desorption process was tested by finding the slopes of plots of log $(i_d - i)/i$ *vs.* E. The desorption did not appear to be reversible, as the slopes of the logarithmic plots were usually about threefold greater than the theoretical value. However, the desorption half-wave potential was independent of the solution tetrachloroplatinate (II) ion concentration, as predicted from the theoretical equation.

The effect of decreasing the average area of adsorption by adding organic materials which are adsorbed on the dropping mercury electrode was studied. It was found that saturated camphor and saturated octyl alcohol shifted the desorption wave markedly in the positive direction. Agar and gelatin had a similar but less pronounced effect.

Tetrachloroplatinate (II) ion gave a normal irreversible reduction wave which had a half-wave potential of — 1.35 volt (*vs.* S.C.E.) for one molar potassium chloride indifferent electrolyte. The half-wave potential shifted to more positive values of e.m.f. as the chloride ion concentration was increased, and it shifted to more negative values as the chloride ion concentration was decreased. The effect of increasing chloride ion concentration in lowering the overvoltage of the irreversible reduction of chloro complexes was observed previously by Lingane (2) for the chloro complex of tin and by Lingane and Nishida (4) for the chloro complex of antimony.

Summary

1. Formulae and dissociation constants of the copper complexes which were shown to be reversibly reduced at the dropping mercury electrode were determined from polarographic data. Pyrophosphate (monohydrogenpyrophosphate) cuprate (II) ion was identified from diffusion current data.

2. The formula and dissociation constant of hydroxopyrophosphatecuprate (II) ion were determined from data obtained with a glass electrode.

3. In the presence of excess ethylenediamine and thiourea, bis (ethylenediamine) copper (II) ion was shown to be reduced in two steps, one electron being added in each electrode reaction.

4. The adsorption phenomenon of tetrachloroplatinate (II) was described, and an equation expressing the desorption half-wave potential was derived. Although the desorption process was not reversible, the desorption half-wave potential was independent of the solution tetrachloroplatinate (II) ion concentration. Added adsorbents shifted the desorption half-wave potential to more positive values of e.m.f.

5. Tetrachloroplatinate (II) ion in one molar potassium chloride showed a normal irreversible reduction wave. The half-wave potential shifted to more positive values of e.m.f. as the chloride ion concentration was increased.

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VITA

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The author has contributed to the following publication:

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